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Fluorescence Study on the Structure of Ionic Liquid Aggregates in Aqueous Solutions

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Abstract Although ionic liquids are a relatively novel class of materials, it is well documented that they form micelles through aggregation of cation aliphatic tails. However, anion self-assembly has not yet been reported. In this study, we analyzed the intrinsic fluorescence of p-toluenesulfonate groups (tosylate) as part of the ionic liquid 1-ethyl-3-methylimidazolium tosylate ([emim][TOS]) and p-toluenesulfonic acid (pTSA), in aqueous solution. pTSA was found to have overlapping monomer and excimer emissions for chromophore concentrations from 10^{-3} to 1 M, whereas [emim][TOS], in the same conditions, showed monomer emission slightly broadened by much weaker excimer emission. These different photophysical behaviors of the same chromophore in the two compounds are explained by the formation of ion pairs by [emim][TOS], which can also be inferred from the loss of vibrational structure of the absorption spectra with respect to pTSA. Despite this different behavior regarding ion pairing, anion aggregation was observed in the excitation spectra of both pTSA and [emim][TOS]. While the absorption spectra corresponded to single chromophores, the excitation spectra changed from those characteristic of a single chromophore (below 10^{-3} M) to red-shifted narrow bands (above 0.1 M) typical of J aggregates. Between those concentrations, the excitation spectra split into blue- and red-shifted bands with relative intensities that changed with concentration as the chromophores rearranged in their clusters from head-to-head to head-to-tail aggregates. Differences between the absorption and excitation spectra were ascribed to aggregation-induced fluorescence enhancement.

Keywords Ionic liquids · Excimer emission · Fluorescence · J aggregates · Head to tail aggregates

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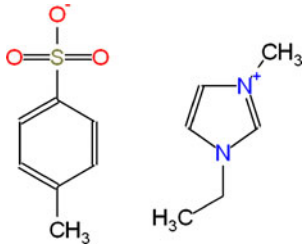
Introduction

In recent years, ionic liquids (ILs) have been the subject of much interest because of their interesting properties and potential applications [1]. ILs are organic salts with melting points below or near room temperature. Despite the large amount of data recently published, there is little information on the structure of IL in the neat or dissolved states, which would aid in understanding their roles in practical applications. ILs form solvent dependent aggregates including clusters, micelles or particles with long range ordering similar to that of surfactants. In this work, we employ the intrinsic fluorescence of p-toluenesulfonate groups (tosylate) to derive molecular-level structural information about the ionic liquid 1-ethyl-3-methylimidazolium tosylate ([emim][TOS], Scheme 1) in aqueous solution, and the results are compared with those of p-toluenesulfonic acid (pTSA).

Fluorescence studies of chromophore-bearing systems are a useful source of dynamic [2, 3] and structural information [4–12]. The fluorescent emission may come from probes or labels added to the system in small enough proportions to avoid modifying the system's macroscopic properties [3, 5–10]. However, these chromophores disturb the local balance of interactions relative to the unlabeled sample, and because they report on local properties rather than on macroscopic properties, they may therefore provide erroneous data. However, these disadvantages can be



Scheme 1 1-Ethyl-3-methylimidazolium tosylate ([emim][TOS])

overcome by taking advantage of the intrinsic fluorescence [2, 7, 8, 10–12] provided by chromophores in an unmodified system and therefore it is preferable to use it when possible.

Fluorescence studies on ILs have been performed by means of fluorescent probes or labels and making use of their intrinsic fluorescence [3–6, 8, 9]. Imidazolium-based ionic liquids that incorporate carbazole or trimethylphenyl moieties showed strong and stable fluorescence [7, 8]. The imidazolium group itself showed weak intrinsic fluorescence that was strongly dependent on the excitation wavelength [13–15]. However, when the imidazolium group was symmetrical, as for 1,3-butylimidazolium chloride [16], the IL was highly fluorescent. Here we consider an IL with a fluorescent anion (tosylate) and cation (imidazolium), although in the selected experimental conditions, only the anion emission was recorded. Among the different ionic liquids investigated, those bearing tosylate anions represent thermodynamically well-characterized systems [17, 18] and are a good, less toxic alternative to halogenated IL.

Experimental Section

p-Toluenesulfonic acid (pTSA) and 1-ethyl-3-methylimidazolium tosylate ([emim][TOS]) were purchased from Sigma-Aldrich and Fluka, respectively. They were used without further purification. Deionized water (MilliQ system from Millipore) was used as solvent.

Steady-state fluorescence spectra were measured in an SLM-Aminco Bowman AB2 spectrometer. Only front face excitation was employed for samples with chromophore concentrations above 0.01 M; the spectra of other samples were measured in both transmission and front face configurations. The excitation and emission bandpasses were kept at 4 nm. The excimer-to-monomer fluorescence ratio (I_E/I_M) was measured as the ratio of the intensities at 320 nm (excimer emission) and 290 nm (monomer emission).

Absorption spectra were measured with a Perkin Elmer Lambda 6 UV/VIS spectrophotometer. The absorption spectra of the most concentrated solutions were observed with 4 mm optical path quartz cuvettes, while 1 cm quartz cuvettes were employed for the diluted solutions.

Results and Discussion

pTSA and [emim][TOS] bear the same chromophore and, therefore, the same photophysical behavior would be expected for both compounds. However, Fig. 1 shows significant differences in the measured emission spectra of their respective aqueous solutions upon excitation at 260 nm. The fluorescence spectra of pTSA dissolved in deionized water had overlapping monomer and excimer bands (Fig. 1a). Monomer emission shifted from 285 to 295 nm with increasing concentration. The excimer band, obtained by subtraction of the spectrum of the most diluted sample (neat monomer emission) from the total spectrum normalized to the same maximum intensity, was centered at 319 nm, which indicates that excimers were weakly stabilized with respect to the monomer excited state [2,11 and references therein]. The excimer to monomer intensity ratio increases with pTSA concentration (Fig. 2) and levels off above 1 M until the whole emission is quenched.

In contrast to pTSA, the fluorescence spectra of [emim][TOS] in aqueous solution (Fig. 1b) had only one band with maximum ranging from 285 to 290 nm and with decreasing intensity for IL concentrations above 1.10^{-2} M. The band broadened with increasing concentration because of incip-

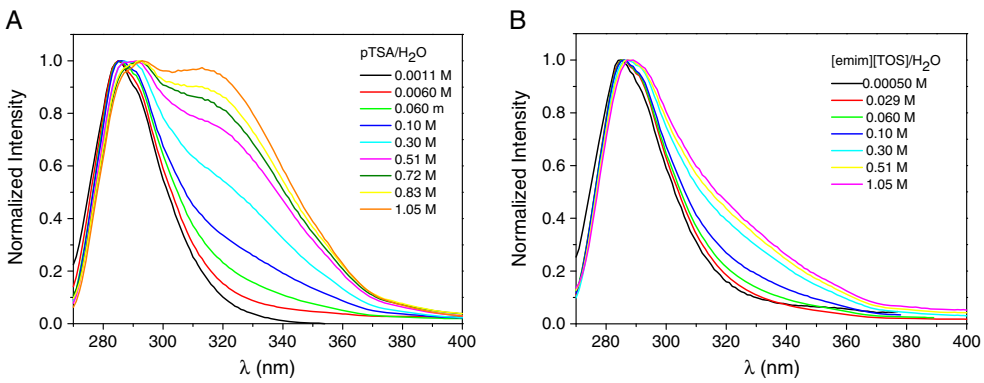


Fig. 1 Normalized fluorescence spectra of pTSA or [emim][TOS] in aqueous solution with different chromophore concentrations, recorded by front face excitation with an excitation wavelength of 260 nm

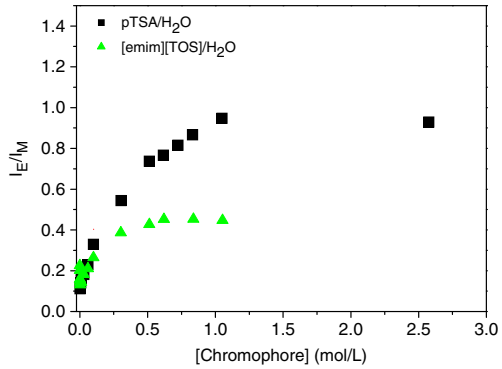


Fig. 2 Excimer-to-monomer fluorescence ratios of [emim][TOS] and pTSA in aqueous solution with different chromophore concentrations upon excitation at 260 nm

ient excimer emission but was more efficiently quenched than pTSA. The fluorescence ratio leveled off at a lower value than pTSA (Fig. 2), suggesting that the capacity for excimer formation was saturated at a lower chromophore concentration. The excimer band of [emim][TOS] was centered at 320 nm, indicating the same excimer configuration as for pTSA.

The two compounds were observed to have the same excimer stability (measured by the red shifts of the excimer bands compared to monomer emission) but different excimer formation capacities (measured by the fluorescence ratios). pTSA is a strong acid totally dissociated in aqueous solution; the volume of its ring substituents and the repulsive interactions of sulfonic groups hinder the formation of anion-anion sandwich-like structures (as excimers). Because of such difficulties, pTSA excimers do not have a perfect sandwich geometry (i.e., either the overlap of aromatic rings is only partial or their planes are not parallel), and thus, their emission is only slightly red shifted with respect to monomer emission. The same holds for tosylate groups of [emim][TOS], i.e., imidazolium cations do not interfere in the anion excimer stability and geometry.

Excimers may be formed by diffusion of single chromophores or by direct absorption of light by ground state dimers or aggregates of larger size [2, 12]. Figure 3a and b show that the excimer contribution to the fluorescence spectra was independent of the excitation wavelength from 240 to 270 nm, except for the largest concentration of pTSA. It denotes that excimers are formed by diffusion of single chromophores rather than excitation of ground state dimers or aggregates, which would have different absorption values than the single chromophores, within that range of excitation wavelengths. On the other hand, the relative contributions of excimer emission increased at longer excitation wavelengths (Fig. 3b), implying that there exist aggregates absorbing from 265 to 280 nm (and even below 250 nm for the largest pTSA concentration) leading to excimer emission with greater efficiency than that of single chromophores. Therefore, we conclude that 1) both single chromophores and tosylate aggregates exist in pTSA and [emim][TOS] aqueous solutions, 2) that they can be excited preferentially with different ranges of excitation wavelengths and 3) pTSA and [emim][TOS] form excimers through diffusion and direct absorption of light, respectively.

The different excimer formation capacities (Fig. 2) by diffusion upon preferential excitation of single chromophores at 260 nm, reveal differences in the local structures of the two compounds. pTSA's larger excimer-to-monomer fluorescence ratio (I_E/I_M) compared to that of [emim][TOS] (Fig. 2) suggests that the proximity of the cations and anions in the IL leads to slower diffusion of both in comparison to the free anions of pTSA. Throughout the monomer excited state lifetime, the tosylate groups of pTSA diffuse a certain distance to encounter a ground state chromophore with which to form an excimer. The distance covered by the ion pairs of [emim][TOS] is shorter because they are larger and their diffusion coefficients are smaller, thus lowering their probability of forming excimers.

The proximity of cation-anion pairs can also be inferred from the losses of vibrational structure in the [emim][TOS] absorption spectra relative to those of pTSA (Fig. 4a and b). Notably, the vibrational resolution was independent of [emim][TOS] concentration, as shown in Fig. 4b. This result concurs with the observed trends of ions preferen-

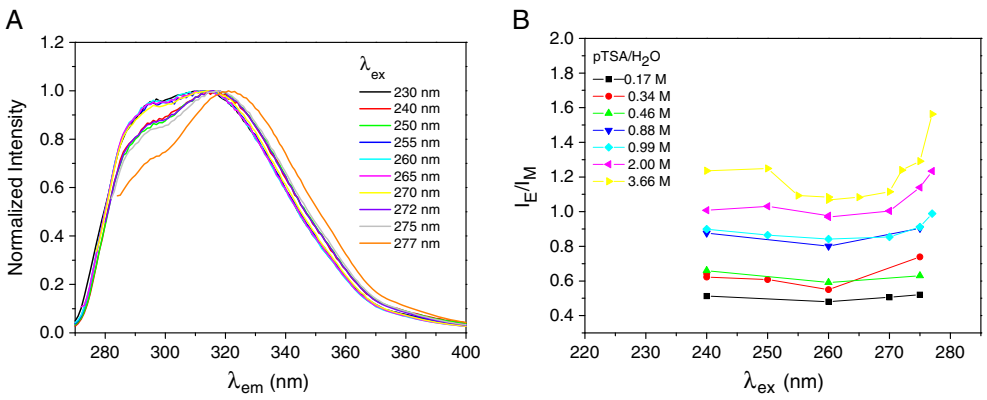


Fig. 3 **a** Normalized fluorescence spectra of pTSA in aqueous solution (3.66 M), measured with different excitation wavelengths. **b** Fluorescence ratio of pTSA in aqueous solution as a function of the excitation wavelength and chromophore concentration

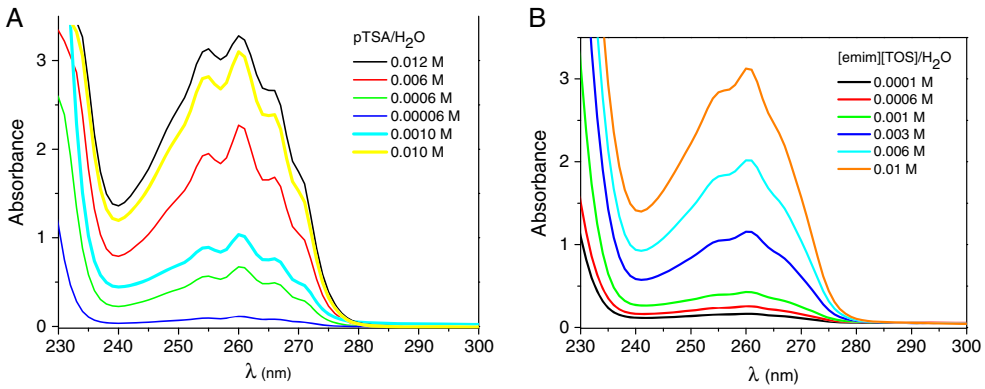


Fig. 4 Absorption spectra of **a**) pTSA and **b**) [emim][TOS] dissolved in deionized water with different concentrations indicated in the insert. An optical path length (OPL) of 1 cm was used for all spectra, except for the two shown in the bottom of the insert whose absorbances were measured with 0.4 cm OPL and divided by 0.4

tially pairing to other ions of similar size (as in [emim][TOS]) over those of disparate size (as in pTSA) [19].

While the constancy of the absorption spectra with concentration (Fig. 4) suggests that the chromophores were molecularly dispersed, the dependence of the shape of the excitation spectra on chromophore concentrations (Fig. 5) indicates aggregation. The absorption spectra of pTSA and [emim][TOS] corresponding to the lowest energy electronic transitions showed a single band centered at 260 nm even at large chromophore concentrations. Contrarily, the excitation spectra showed two bands with positions and relative intensities that were highly dependent on chromophore concentration.

Qualitatively, the excitation spectra of [emim][TOS] and pTSA in deionized water show the same dependence on concentration. Figure 5a and b illustrate this dependence in the whole range of concentrations here employed, making use of [emim][TOS] for the limit of low concentrations and pTSA for the upper limit. The excitation spectra of [emim][TOS] and pTSA in very diluted solutions (chromophore concentrations of less than 10–3 M) contained a band centered at 260 nm that was coincident with the absorption spectra, together with a blue side band (Fig. 5a). The band at 260 nm corresponds to the absorption of individually dispersed chromophores and its intensity increased with concentration in that range, while the blue side band decreased as it was red shifted. Above 10^{-3} M, the excitation and absorption spectra behaved separately. While the shape of the absorption spectra did not change with concentration for chromophore concentrations around 10^{-2} M, a new band emerged on the red side of the excitation spectra below the original band at 260 nm. The blue and red side bands shifted bathochromically (Fig. 5) and the intensity of the red side band increased while the blue side band tended to disappear in the base line.

Changes of the excitation spectra with chromophore concentration are evidence of aggregation and aggregation-induced emission enhancement [20–22]. Since most chromophores are molecularly dissolved, the shape of the absorption spectra did not change with concentration for [emim][TOS] or pTSA. Nevertheless, the emission of those single chromophores (excited at 260 nm) is rapidly quenched at concentrations above 10^{-2} M for both compounds. The small fraction of chromophores in aggregates has a negligible contribution to the red and blue edges of the absorption spectra but they are efficiently fluorescent

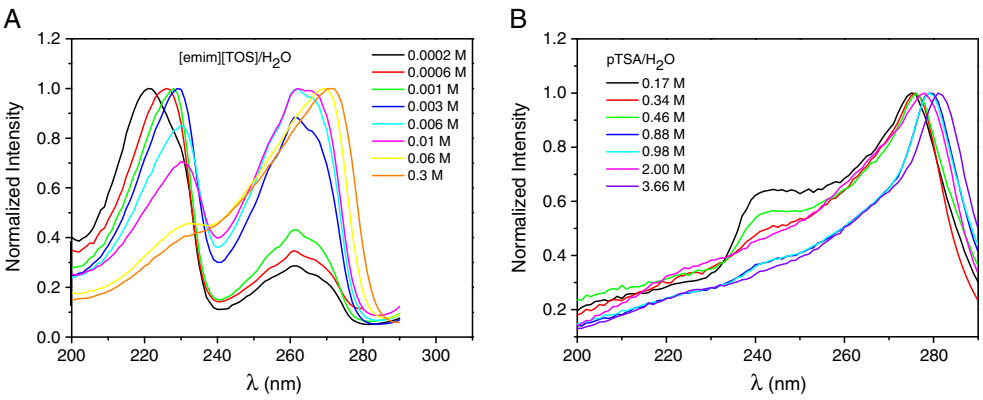


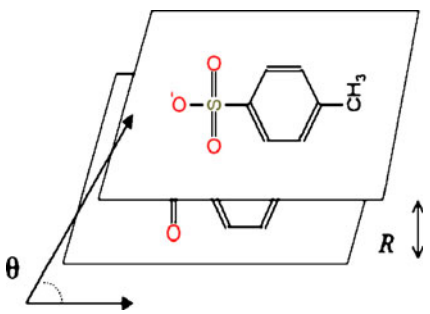
Fig. 5 Representative excitation spectra of [emim][TOS] and pTSA in aqueous solution, normalized to the maximum intensity, with emission wavelength fixed at 300 nm and 350 nm respectively. Plot A illustrates the behavior of the most diluted samples and plot B that of the concentrated solutions

because their non-radiative decay is inhibited. On top of 10^{-2} M, the aggregates dominate the excitation and emission spectra even though they are not yet relevant in the absorption spectra which means that fluorescence is enhanced by aggregation.

The formation of J and H aggregates helps to explain this behavior [23, 24]. Planar molecules tend to form aggregates with parallel arrangements. When two identical chromophores in the ground state come into close proximity, excitonic coupling causes a shift of the absorption spectrum that depends on the relative dipole orientations. Parallel orientations with head-over-head orientations (H or sandwich-like aggregates) result in a blue shift, while linear head-to-tail orientations (J aggregates) cause a red shift. The intermediate oblique orientation produces band splitting with two bands appearing at lower and higher energies [23]. Because J structures are more exposed to solvent than H aggregates, the preference of a given molecule for the J or H structure depends on the driving force for aggregation.

Commonly, the fluorescence of J aggregates is intense and appears as a resonant emission at nearly the same wavelength as the bathochromically shifted narrow and intense absorption peak. In contrast, H aggregates are weak or non-fluorescent. The blue and red side bands of the tosylate excitation spectra possess characteristics attributable to the absorption of H and J aggregates (respectively) with the particularity that upon excitation with wavelengths of those bands (Fig. 3), the fluorescence spectra of pTSA and [emim][TOS] exhibit not only monomer emission (as for common dyes) but also excimer emission.

Within this type of anion clusters (Scheme 2) the aromatic rings are disposed in parallel planes at an intermolecular distance R and twisted at an angle θ. The slip angle θ, is the angle between the line of centers of a stack of molecules and the long molecular axis of any of the parallel molecules. It is related to the relative values of f_1 and f_2, the areas under the blue (f_2) and red (f_1) side absorption bands of aggregates, which are normally difficult to resolve [23]. Fortunately, here they can be identified with the corresponding bands of the tosylate excitation spectra, which were well resolved in most cases.



Scheme 2 Geometrical characteristics of tosylate assemblies with intermediate structures between those of pure J and H aggregates

The slip angle changes in the different ranges of tosylate concentration. H aggregates correspond to θ=90° or f_1/f_2= 0, and they were observed only in very diluted solutions (chromophore concentrations below 6.10^{-3} M). In that range, the red side band, if it existed, was hidden below the absorption of single chromophores (which were predominant, Fig. 5a) and since this band's shape was not distorted, pure or almost pure H aggregates were likely formed in these cases.

Above that concentration, in the range 10^{-3} to 10^{-1} M, the red side band overlapped with the absorption of single chromophores and its intensity was similar to that of the blue side band; f_1/f_2 increases from below 1 to above 1 (Fig 5a and b) and therefore, the aggregated tosylate groups tilt progressively, tending to align with each other with θ= 0°. At concentrations above 10^{-1} M, the absorption of single chromophores at 260 nm and the blue side band disappeared (f_2=0), indicating the formation of pure J aggregates.

Conclusion

The fluorescence spectra of aqueous pTSA solutions with chromophore concentrations from 10^{-3} to 1 M and excitation wavelengths from 240 to 280 nm contained overlapping monomer and excimer emissions. The proximity of the observed monomer and excimer emissions indicates that the parallel chromophore stacking inherent to excimer formation is hindered by aromatic ring substituents and repulsive electrostatic interactions between sulfonate groups. In the case of [emim][TOS], the excimers have the same stability, i.e., imidazolium cations do not interfere in the excimer geometry. However, the excimer to monomer fluorescence ratio was lower for [emim][TOS] than for pTSA because excimer formation through diffusion of [emim][TOS] is hampered by the formation of ionic pairs, which are also observed as a loss of vibrational resolution of the absorption spectra.

Despite this different behavior in emission, anion aggregation was observed both for pTSA and [emim][TOS]. While the absorption spectra corresponded to single chromophores, the excitation spectra changed from those of single chromophores (below 10^{-3} M) to red-shifted narrow bands (above 0.1 M) typical of J aggregates.. Between those concentrations, the excitation spectra split into blue- and red-shifted bands with relative intensities that changed with concentration as the chromophores rearranged from head-to-head to head-to-tail aggregates. The coincident behaviors of pTSA and [emim][TOS] indicate that anion aggregation is not hindered by protons or cations. We

therefore conclude that aggregation is driven exclusively by anion hydrophobic interactions.

While aggregates were not observed in the absorption spectra, they dominated the excitation spectra. Differences between the absorption and excitation spectra were ascribed to aggregation-induced fluorescence enhancement; only a very small fraction of the chromophores form aggregates, but their emission is much more intense than that of single chromophores.

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